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PREPARATION AND CHARACTERIZATION OF THE QUATERNARY
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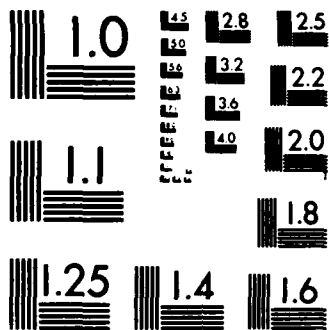
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Preparation and Characterization of the Quaternary Chalcogenides

$\text{Cu}_2\text{B(II)C(IV)X}_4$ [B(II) = Zn, Cd; C(IV) = Si, Ge; X = S, Se]

by

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 $\text{Cu}_2\text{B(II)C(IV)X}_4$ [B(II) = Zn,Cd; C(IV) = Si,Ge; X = S,Se]

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A number of quaternary chalcogenides crystallizing with the wurtz-stannite structure have been prepared by chemical vapor transport and characterized. $\text{Cu}_2\text{ZnGeS}_4$ and $\text{Cu}_2\text{ZnSiSe}_4$ transmit in the infrared beyond 12 microns. $\text{Cu}_2\text{ZnGeS}_4$ was stable in air up to 620°C and also was the hardest of all the materials studied.

1. INTRODUCTION

In recent years, compounds crystallizing with the chalcopyrite structure have been studied in order to observe their optical and semiconducting properties. However, only a relatively few studies have been reported concerning the characterization of quaternary chalcogenides crystallizing with the stannite structure. The compounds $\text{Cu}_2\text{ZnSiS}_4$, $\text{Cu}_2\text{ZnSiSe}_4$, $\text{Cu}_2\text{ZnGeS}_4$ and $\text{Cu}_2\text{CdSiS}_4$ are semiconductors which crystallize with the orthorhombic superstructure of wurtzite called the wurtz-stannite structure (1-4) space group $\text{Pmn}2_1$, shown in Fig. 1. In this structure there are alternating cation layers of mixed B(II) and C(IV) atoms, which are separated by layers of Cu atoms. The structure is therefore derived from an ordering of the cations of the wurtzite cell. In this structure, every sulfur or selenium has four nearest neighbor metal atoms at the corners of the surrounding tetrahedron, two copper atoms, one zinc or cadmium atom, and either a silicon or germanium atom.

Single crystals of these compounds have been grown by chemical vapor transport using iodine as the transport agent (1-4). Several publications report their magnetic, electrical and optical properties (4-6). However, there has been no report concerning their hardness, thermal stability or their transmission in the infrared. It was of interest to measure these properties and correlate them with the substitutions made for the Group II, Group IV and Group VI elements.

2. EXPERIMENTAL

Single crystal growth.

Single crystals of the quaternary chalcogenides were all prepared by chemical vapor transport using iodine as the transport agent. The stoichiometric weights of the elements were introduced into silica tubes which were evacuated to 5×10^{-5} torr. Five mg/cc of iodine were added to the transport tube which was then sealed and the tube set in the back transport mode and run in this mode for two days. Optimum crystal growth of $\text{Cu}_2\text{ZnGeS}_4$,

$\text{Cu}_2\text{CdSiS}_4$, $\text{Cu}_2\text{ZnSiSe}_4$ occurred when the charge zone was maintained at 850°C and the growth zone at 800°C . The transport temperature was 950°C at the charge zone and 900°C at the growth zone for crystal growth of $\text{Cu}_2\text{ZnSiS}_4$. The transport process was carried out for two weeks. Polyhedral crystals $2 \times 2 \times 3 \text{ mm}^3$ of $\text{Cu}_2\text{ZnGeS}_4$ and blade crystals $2 \times 1 \times 7 \text{ mm}^3$ of $\text{Cu}_2\text{ZnSiS}_4$, $\text{Cu}_2\text{ZnSiSe}_4$ and $\text{Cu}_2\text{CdSiS}_4$ were obtained.

Powder diffraction patterns of ground single crystals were obtained with a Norelco diffractometer using monochromatic radiation from a high-intensity copper source ($\lambda\text{-CuK}\alpha_1 = 1.5405\text{\AA}$). Cell parameters were determined from slow-scan ($0.25^\circ/\text{min}$) diffraction patterns over the range $12^\circ < 2\theta < 72^\circ$. The precise cell parameters were obtained using a least-squares refinement from these reflections.

Optical and electrical measurements.

Infrared transmission measurements were made on polished single-crystal slices at room temperature using a Perkins-Elmer 580 single beam scanning infrared spectrophotometer. The measurements were performed in the transmission mode over the range $2.5\mu\text{m} - 25\mu\text{m}$. Transmission through the sample was normalized to the signal obtained in the absence of the sample.

Measurements of absorption coefficients were made with an Oriel Model 1724 monochromator, an Oriel G 772-5400 long pass filter, and a calibrated silicon diode detector. Absorption values were calculated from the responses with and without the crystal in the beam.

The van der Pauw (7) method was used to measure electrical resistivities from 77K to 400K. Contacts were made by the ultrasonic soldering of indium onto the samples, and ohmic behavior was established by measuring the current-voltage characteristics.

3. RESULTS AND DISCUSSION

Single crystals of $\text{Cu}_2\text{ZnSiS}_4$, $\text{Cu}_2\text{ZnSiSe}_4$, $\text{Cu}_2\text{ZnGeS}_4$, $\text{Cu}_2\text{CdSiS}_4$, $\text{Cu}_2\text{ZnGeSe}_4$ and $\text{Cu}_2\text{CdGeSe}_4$ have been grown by chemical vapor transport using iodine as the transport agent. The first

four compounds showed transmission in the infrared region and were therefore studied in detail. A relatively high transport temperature (950°C - 900°C) was used to grow $\text{Cu}_2\text{ZnSiS}_4$ single crystals because at lower temperatures (850°C - 800°C) the major phase obtained at the growth zone was ZnS.

X-ray diffraction analysis confirmed the cell parameters (Table 1) of these quaternary chalcogenides previously reported (3, 4, 6).

The microhardness measurements (Knoop indenter) were made on crystals using a Kentron Microhardness Tester. The results were obtained using a diamond indenter with a 100 g load and are given in Table 1.

The stability of these compounds toward oxidation was determined by heating them in a flowing oxygen stream (65 cc/min) and determining the change in weight during the heating period. The results shown in Table 1 indicate that $\text{Cu}_2\text{ZnSiS}_4$ decomposes at a higher temperature than the selenide $\text{Cu}_2\text{ZnSiSe}_4$. Furthermore $\text{Cu}_2\text{ZnSiS}_4$ is more stable than $\text{Cu}_2\text{CdSiS}_4$. A comparison of the relative thermal stability of $\text{Cu}_2\text{ZnSiS}_4$ and $\text{Cu}_2\text{ZnGeS}_4$ is shown in Fig. 2. It can be seen that the rate of oxidation proceeds much slower for the former compound. These results are consistent with the anticipated increased stability of sulfides vs selenides and silicon vs germanium or zinc vs cadmium chalcogenides.

A comparison of the infrared absorption bands can also be made by examining the results summarized in Table 1 and Figs. 3 and 4. It can be seen that the substitution of selenium for sulfur shifts the absorption bands to higher wavelengths. The substitution of germanium for silicon also results in a shift of the bands to higher wavelengths but in addition the absorption peaks occur much closer together.

The indirect optical band gaps were obtained from plots of $(\alpha h\nu)^{1/2}$ vs energy and are given in Table 1. $\text{Cu}_2\text{ZnSiS}_4$ was observed to show the largest band gap (3.04 eV) and there was a marked decrease in the band gap when either a larger cation (Cd or Ge) or anion (Se) was substituted for Zn, Si or S. The resistivities

for the four chalcogenides are also given in Table 1 and the lower resistivity of the cadmium compound is consistent with the electronic properties of other cadmium chalcogenides.

4. ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Fig. 1.

The wurtz-stannite structure.

Fig. 2.

Comparison of the stability toward oxidation in O_2 of ground crystals of Cu_2ZnSiS_4 and Cu_2ZnGeS_4 .

Fig. 3.

Comparison of the infrared transmission spectra of polished crystals of Cu_2ZnSiS_4 and $Cu_2ZnSiSe_4$, normalized to a thickness of 0.11 mm assuming no reflection or scattering.

Fig. 4.

Comparison of the infrared transmission spectra of polished crystals of Cu_2ZnSiS_4 and Cu_2ZnGeS_4 , normalized to a thickness of 0.11 mm assuming no reflection or scattering.

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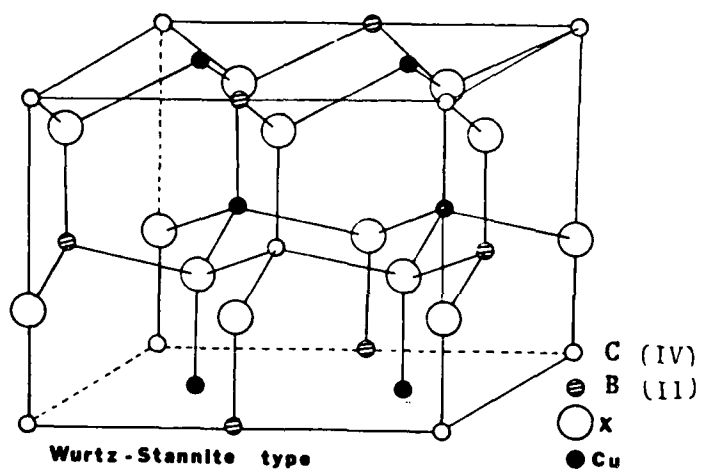
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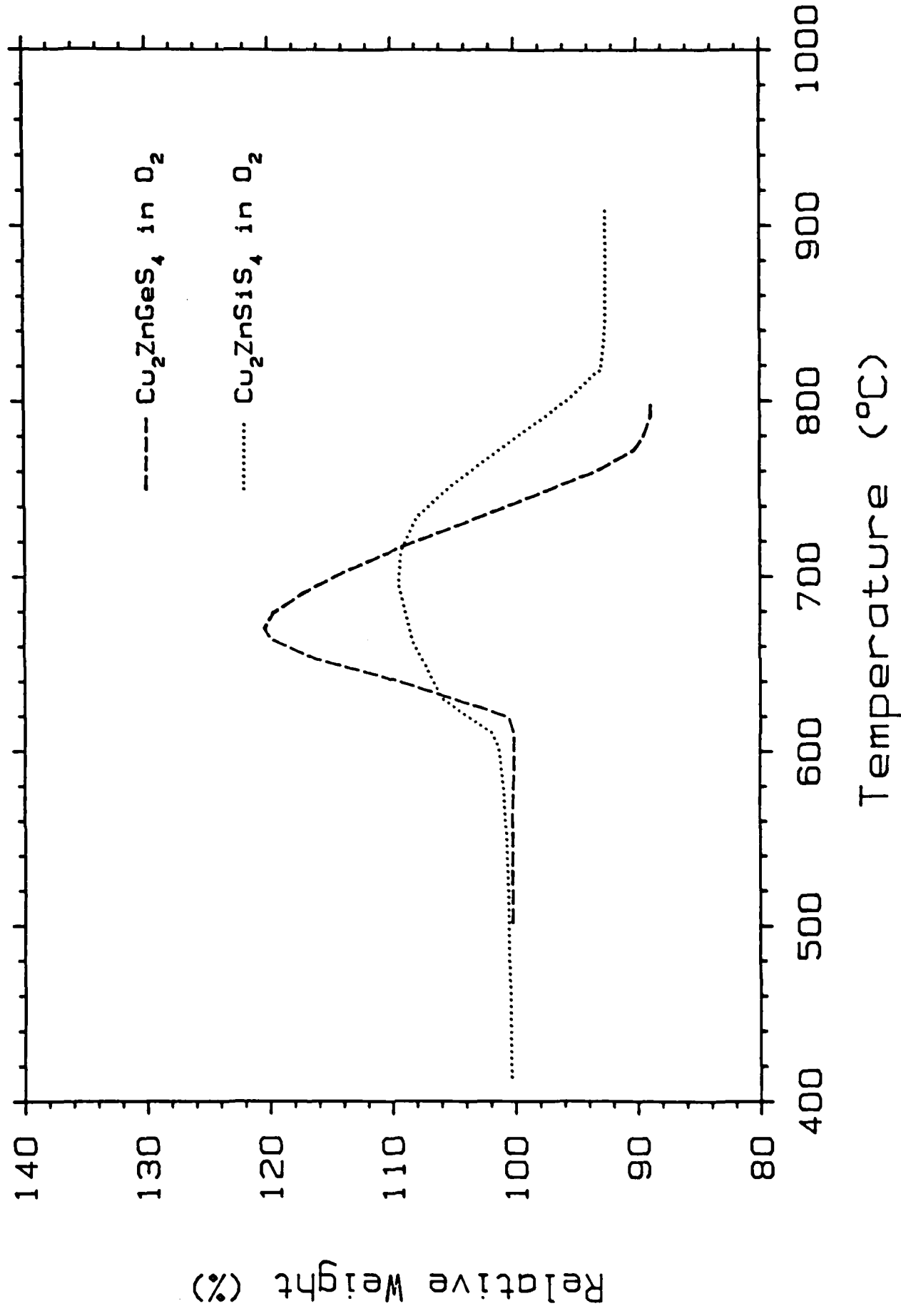
TABLE 1. PROPERTIES OF SOME QUATERNARY CHALCOGENIDES

Compound	Cell Parameter		(R-T) (Ω -cm)	E _g (e.v.)	IR Absorption bands (μ)	Knoop* Hardness kg/mm ²	Decomposition Temperature C° \pm 10)
Cu ₂ ZnSiS ₄ (orth)	A	B	C				
	7.436(1)	6.398(1)	6.137(2)	Insulator	3.04(2)	7.9(w) 9.7, 11.1	620
Cu ₂ ZnGeS ₄ (orth)	A	B	C				
	7.506(3)	6.476(4)	6.189(2)	1.6 x 10 ⁴	2.04(2)	12.6, 13.2	620
Cu ₂ ZnSiSe ₄ (orth)	A	B	C				
	7.826(3)	6.727(2)	6.445(1)	3 x 10 ⁴	2.20(2)	12, 15.3	470
Cu ₂ CdSiS ₄ (orth)	A	B	C				
	7.609(1)	6.485(1)	6.251(1)	48	2.0 2.45(5)	9.7, 11.1 12.5(w)	510

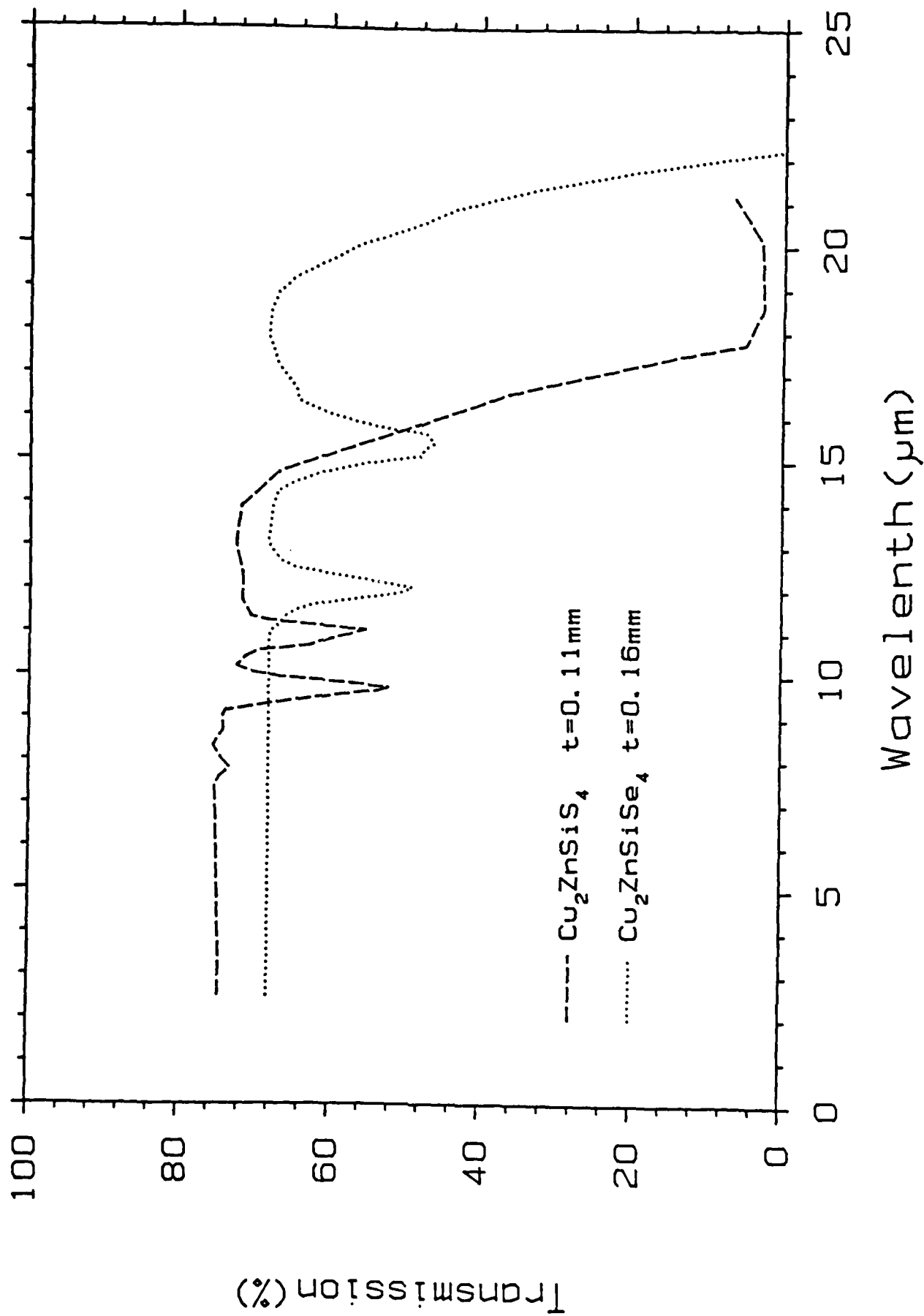
*Knoop indenter at 100g, lowered slowly. Hardness values \pm 100.



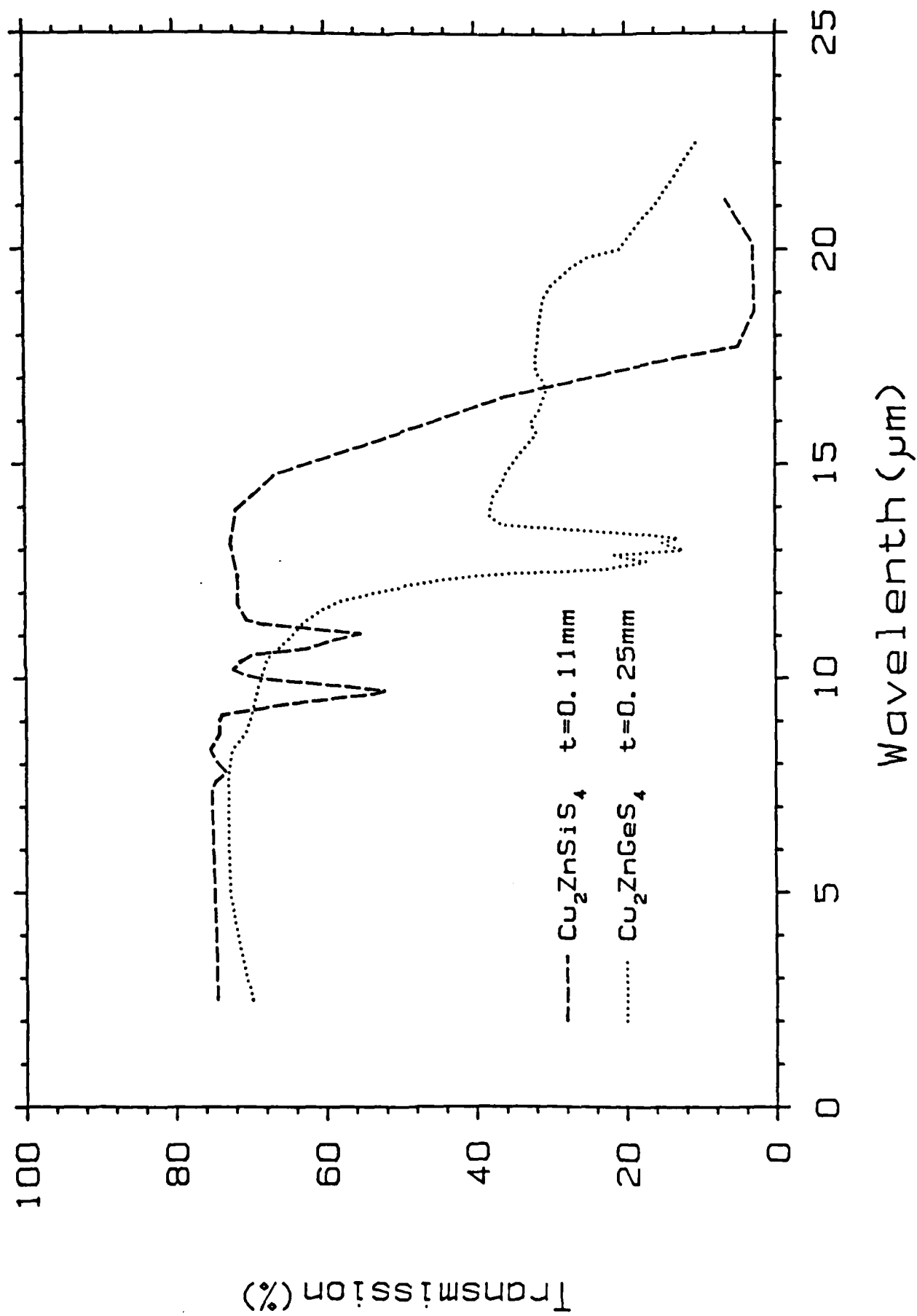
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